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(71) Applicant (*for all designated States except US*): **SYNGENTA LIMITED** [GB/GB]; European Regional Centre, Priestley Road, Surrey Research Park, Guildford, Surrey GU2 7YH (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BELL, Gordon**, Alastair [GB/GB]; Syngenta Limited, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6EY (GB). **HART, Clifford, Arthur** [GB/GB]; Syngenta Limited, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6EY (GB). **MURFITT, Roger, Cyril** [GB/GB]; Syngenta Limited, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6EY (GB). **SUTTON, Peter, Bernard** [GB/GB]; Syngenta Limited, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6EY (GB).

(74) Agents: **RICKS, Michael, James et al.**; Intellectual Property Department, Syngenta Limited, P.O. Box 3538, Jealott's Hill Research Centre, Bracknell, RG42 6YA (GB).

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(54) Title: **NOVEL COMPOUNDS**

(57) Abstract: An adjuvant suitable for use with a lipophilic agrochemical has the formula (I),  $R_1-(CO)_m-O-[-R_2O-]_n-R_3$ , wherein  $R_1$  is a  $C_{16}$  to  $C_{20}$  straight or branched chain alkyl or alkenyl group,  $R_2$  is ethyl or isopropyl,  $n$  is from 8 to 30 and  $m$  is 0 or 1 and when  $R_2$  is ethyl,  $R_3$  is a  $C_1$  to  $C_7$  alkyl group and when  $R_2$  is isopropyl,  $R_3$  is hydrogen or a  $C_1$  to  $C_7$  alkyl group, provided that when  $R_1$  is oleyl,  $R_2$  is isopropyl and  $R_3$  is hydrogen,  $n$  is not 10. An adjuvant composition comprising an agrochemical and an adjuvant of formula (I) is also claimed. Adjuvants of the invention show effective bioperformance enhancement despite having little or no surfactant properties.

## NOVEL COMPOUNDS

This invention relates to novel compounds and in particular to novel adjuvants and to their use in agrochemical formulations.

5 A wide variety of adjuvants are available to those skilled in the art for the improvement of the bioperformance of active ingredients such as agrochemicals. In addition to the effect on bioperformance, the physical properties of an adjuvant are of key importance and must be selected with a view to compatibility with the formulation concerned. Thus by way of a single example, it is generally simpler to incorporate a solid adjuvant into a solid  
10 formulation such as a water-soluble or water-dispersible granule. In general adjuvants rely on surfactant properties for bioperformance enhancement and one typical class of adjuvants involves an alkyl or aryl group to provide a lipophilic moiety and a (poly) ethoxy chain to provide a hydrophilic moiety. Much has been published on the selection of adjuvants for various purposes and in Hess, F.D. and Foy, C.L., Weed technology, 2000, 14, 807-813 for  
15 example it is disclosed that adjuvants for use with lipophilic agrochemical active ingredients are generally of relatively low molecular weight with a degree of ethoxylation which leads to a hydrophile lipophile balance (HLB) of 8 or less. This corresponds to a surfactant with 12 carbon atoms in the lipophilic chain and between 2 and 3 moles of ethoxylate in the hydrophilic portion of the adjuvant. Similarly a surfactant with a longer carbon chain, such  
20 as 18 atoms, would have four or less moles of ethoxylate.

Propoxylate groups are considered to be lipophilic. A molecule with a hydrocarbon chain and propoxylate groups would not be considered to have an HLB value and would normally not be considered as a surfactant.

Particular care is required when selecting bioperformance enhancing adjuvants for  
25 incorporation in a microencapsulated presentation of an active ingredient, since many conventional ethoxylated adjuvants interfere with the microcapsule wall-forming reaction at the oil/water interface. Use of such adjuvants results in weak or ruptured microcapsules and their presence is therefore undesirable.

In GB 2024626 there is disclosed a range of polypropylene glycol derivatives suitable  
30 for destroying mites or ectoparasites and their eggs. In Table 3 there is disclosed propoxylated (10) oleyl alcohol.

We have now found that certain novel alkoxylated long-chain alcohols and acids and end-capped variants thereof, despite having little or no surfactant properties, are

unexpectedly effective bioperformance enhancing adjuvants and furthermore have physical properties and attributes that render them particularly effective in certain formulation vehicles.

According to the present invention there is provided an adjuvant having the  
5 formula (I)



wherein  $R_1$  is a  $C_{16}$  to  $C_{20}$  straight or branched chain alkyl or alkenyl group,  $R_2$  is ethyl or isopropyl,  $n$  is from 8 to 30 and  $m$  is 0 or 1 and when  $R_2$  is ethyl,  $R_3$  is a  $C_1$  to  $C_7$  alkyl group and when  $R_2$  is isopropyl,  $R_3$  is hydrogen or a  $C_1$  to  $C_7$  alkyl group, provided that when  $R_1$  is  
10 oleyl,  $R_2$  is isopropyl and  $R_3$  is hydrogen,  $n$  is not 10.

According to a further aspect of the present invention there is provided an agrochemical composition comprising a herbicide or fungicide and an adjuvant having the formula (I)



15 wherein  $R_1$  is a  $C_{16}$  to  $C_{20}$  straight or branched chain alkyl or alkenyl group,  $R_2$  is ethyl or isopropyl,  $n$  is from 8 to 30 and  $m$  is 0 or 1 and when  $R_2$  is ethyl,  $R_3$  is a  $C_1$  to  $C_7$  alkyl group and when  $R_2$  is isopropyl,  $R_3$  is hydrogen or a  $C_1$  to  $C_7$  alkyl group.

The agrochemical is preferably a lipophilic herbicide or fungicide..

When  $R_1$  is an alkenyl group it may have one or more double bonds which may be in  
20 either cis or trans configuration(s). Preferably  $R_1$  has from 1 to 3 double bonds. It is generally preferred that the double bond(s) are in the cis configuration. It is especially preferred that  $R_1$  is a  $C_{18}$  branched chain alkyl or  $C_{18}$  alkenyl group for example oleyl or isostearyl (derived from the alcohol, 2-hexyl-dodecan-1-ol).

The value of  $n$  is preferably from 10 to 30 and especially from 10 to 20. The value of  
25  $n$  may be an integer when a specific and uniform number of groups  $R_2O$  are introduced or may be an average value when a range of numbers of such groups are introduced.

The value of  $m$  is preferably 0.

When  $R_3$  is not hydrogen it is preferably a  $C_1$  to  $C_4$  alkyl group and in particular methyl or butyl. Butyl is especially preferred. Those skilled in the art will appreciate that an  
30 alkyl group  $R_3$  represents an "end cap" to the terminal hydroxyl of the group



Since "end capping" a terminal ethylene oxide group ( $R_2$  is ethyl) removes certain undesirable properties (such as the interference with the microencapsulation process) as

discussed herein, it is desirable in order to achieve the objects of the invention to "end cap" substantially all of the terminal hydroxyl groups when  $R_2$  is ethyl. Thus  $R_3$  is not hydrogen when  $R_2$  is ethyl. When  $R_2$  is isopropyl on the other hand,  $R_3$  may be hydrogen or alkyl since both moieties achieve the objects of the invention. It is thus possible to "end cap" only a proportion of the terminal hydroxyl groups such that  $R_3$  is a mixture of hydrogen and alkyl groups.

We have found that both propoxylated oleyl and isostearyl alcohols (when the value of  $m$  is 0) and acids (when the value of  $m$  is 1) and their end-capped equivalents show no significant surfactant properties. These materials do not contain a hydrophilic moiety and would not be considered to have an HLB classification. Attempts to use these materials to emulsify a simple oil such as decane into water showed that separation into two phases occurred even after vigorous shaking. Where some small amount of emulsification was observed this was found to be short lived. . Surprisingly the bioperformance enhancement, in particular for lipophilic agrochemicals, is excellent despite the lack of surfactant properties. Moreover, the absence of surfactant properties may bring a number of advantages such as reduced spray drift, a reduction in adverse interaction with surfactants added for formulation purposes (such as suspension of a dispersed solid) and reduced gelling of the formulation. Moreover the adjuvants are generally liquids (oils) which are substantially insoluble in water and are readily compatible for example with emulsion concentrates in which they dissolve in the oil phase. They are also more readily used as stand-alone tank mix adjuvants since they are oil-soluble. Increasing the molecular weight, for example using butyl end-capping and a value of  $n$  towards the upper end of the range, may produce a solid adjuvant which is for example well adapted for incorporation in solid formulations such as water-soluble or water-dispersible granules. In general the propoxylated adjuvants of the present invention are liquid whereas the ethoxylates are either solid or semi-solid. An exception is oleyl 10 EO with a butyl end cap which is a liquid.

We have found similarly that ethoxylated oleyl and isostearyl end-capped methyl and butyl ethers show no significant surfactant properties. They generally have different physical properties from the uncapped equivalents which can be used to advantage. For example oleyl 10 EO end-capped butyl ether is an oily liquid which emulsifies readily in water whilst the uncapped oleyl 10 EO equivalent forms viscous liquid crystals on contact with water. Increasing the molecular weight, for example using butyl end-capping and a value of  $n$  towards the upper end of the range, may produce a solid adjuvant which is for

example well adapted for incorporation in solid formulations such as water-soluble or water-dispersible granules. Typical of such a solid adjuvant according to the present invention is oleyl 20 EO end-capped with butyl (i.e. the compound in which R<sub>1</sub> is oleyl, R<sub>2</sub> is ethyl, n is 20 and R<sub>3</sub> is butyl).

5           As specific examples of the adjuvants of the present invention or which may be used in agrochemical compositions of the present invention there may be mentioned oleyl 10 propylene oxide (i.e. a compound of Formula (1) wherein R<sub>1</sub> is oleyl, m is 0, R<sub>2</sub> is isopropylene, n is 10 and R<sub>3</sub> is hydrogen), oleyl 10 propylene oxide end-capped butyl ether (i.e. a compound of Formula (1) wherein R<sub>1</sub> is oleyl, m is 0, R<sub>2</sub> is isopropylene, n is 10 and  
10   R<sub>3</sub> is butyl), oleyl 20 propylene oxide, oleyl 20 propylene oxide end-capped butyl ether, isostearyl 10 propylene oxide, isostearyl 20 propylene oxide, oleyl 10 ethylene oxide end-capped butyl ether, oleyl 20 ethylene oxide end-capped butyl ether, oleic acid 10 ethylene oxide end-capped methyl ether (i.e. a compound of Formula (1) wherein R<sub>1</sub> is oleyl, m is 1, R<sub>2</sub> is ethylene, n is 10 and R<sub>3</sub> is methyl), oleic acid 20 ethylene oxide end-capped methyl  
15   ether.

Adjuvants of the present invention are generally compatible with microencapsulation processes and can be incorporated as bioperformance enhancing adjuvant in a microencapsulated agrochemical formulation without detriment to the microcapsule properties. In contrast conventional ethoxylated alcohol surfactants tend to interfere with  
20   interfacial polymerisation wall-forming processes which are key to most conventional microencapsulation processes.

Adjuvants of the present invention have a variety of uses but are particularly suitable for enhancing the bioperformance of lipophilic agrochemicals, including herbicides, fungicides and insecticides. Examples of suitable lipophilic agrochemicals include  
25   herbicides such as fluzifop, mesotrione, fomesafen, tralkoxydim, napropamide, amitraz, propanil, cyprodanil, pyrimethanil, dicloran, tecnazene, toclofos methyl, flamprop M, 2,4-D, MCPA, mecoprop, clodinafop-propargyl, cyhalofop-butyl, diclofop methyl, haloxyfop, quizalofop-P, indol-3-ylacetic acid, 1-naphthylacetic acid, isoxaben, tebutam, chlorthal dimethyl, benomyl, benfuresate, dicamba, dichlobenil, benazolin, triazoxide, fluazuron,  
30   teflubenzuron, phenmedipham, acetochlor, alachlor, metolachlor, pretilachlor, thenylchlor, alloxymid, butoxydim, clethodim, cyclodim, sethoxydim, tepraloxymid, pendimethalin, dinoterb, bifenox, oxyfluorfen, acifluorfen, fluoroglycofen-ethyl, bromoxynil, ioxynil, imazamethabenz-methyl, imazapyr, imazaquin, imazethapyr, imazapic, imazamox,



flumioxazin, flumiclorac-pentyl, picloram, amodosulfuron, chlorsulfuron, nicosulfuron, rimsulfuron, triasulfuron, triallate, pebulate, prosulfocarb, molinate, atrazine, simazine, cyanazine, ametryn, prometryn, terbuthylazine, terbutryn, sulcotrione, isoproturon, linuron, fenuron, chlorotoluron, metoxuron, 8-(2,6-diethyl-4-methyl-phenyl)tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione and 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester, fungicides such as azoxystrobin, trifloxystrobin, kresoxim methyl, famoxadone, metominostrobin, picoxystrobin, dimoxystrobin, fluoxastrobin, orysastrobin, metominostrobin, prothioconazole, carbendazim, thiabendazole, dimethomorph, vinclozolin, iprodione, dithiocarbamate, imazalil, prochloraz, fluquinconazole, epoxiconazole, flutriafol, azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, hexaconazole, paclobutrazole, propiconazole, tebuconazole, triadimefon, triticonazole, fenpropimorph, tridemorph, fenpropidin, mancozeb, metiram, chlorothalonil, thiram, ziram, captafol, captan, folpet, fluazinam, flutolanil, carboxin, metalaxyl, bupirimate, ethirimol, and insecticides such as thiamethoxam, imidacloprid, acetamiprid, clothianidin, dinotefuran, nitenpyram, fipronil, abamectin, emamectin, bendiocarb, carbaryl, fenoxycarb, isoprocarb, pirimicarb, propoxur, xylylcarb, asulam, chlorpropham, endosulfan, heptachlor, tebufenozide, bensultap, diethofencarb, pirimiphos methyl, aldicarb, methomyl, cyprmethrin, bioallethrin, deltamethrin, lambda cyhalothrin, cyhalothrin, cyfluthrin, fenvalerate, imiprothrin, permethrin, halfenprox.

Adjuvants of the present invention may be prepared by conventional techniques. Thus for example the ethoxylated or propoxylated alcohol or acid may be manufactured by base catalysed condensation of the relevant alcohol or acid (for example oleyl or isostearyl alcohol or acid) with ethylene oxide (or propylene oxide as the case may be). End-capped derivatives may be obtained by reacting the ethoxylated or propoxylated alcohol or acid with the appropriate alkyl halide (for example butyl chloride) in the presence of a base.

The proportion of adjuvant relative to active ingredient can readily be selected by one skilled in the art to meet the intended utility. Typically the ratio of adjuvant to active ingredient will range from 1:50 and 200:1 and preferably from 1:5 to 20:1

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

## EXAMPLES 1 to 10

Compounds of the present invention or for use in agrochemical compositions of the present invention are characterised as indicated below. In each case NMR spectra were run as 10 % v/v solutions in CDCl<sub>3</sub> on a Varian Inova 400 spectrometer. A bold and underlined

5 hydrogen indicates the hydrogen responsible for the relevant signal.

**Oleyl 10 propylene oxide**

	$\delta$ 5.34	multiplet	2H	oleyl 9 & 10CH
	$\delta$ 4 - 3	multiplet	32H	oleyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
	$\delta$ 2.01	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
10	$\delta$ 1.56	multiplet	2H	oleyl 2CH <sub>2</sub>
	$\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
	$\delta$ 1.14	multiplet	30H	propoxylate 3CH <sub>3</sub>
	$\delta$ 0.88	triplet J=6.9Hz	3H	oleyl 18CH <sub>3</sub>

**Oleyl 10 propylene oxide end-capped butyl ether**

15	$\delta$ 5.34	multiplet	2H	oleyl 9 & 10CH
	$\delta$ 4 - 3	multiplet	34H	butyl 1CH <sub>2</sub> , oleyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
	$\delta$ 2.02	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
	$\delta$ 1.55	multiplet	4H	oleyl 2CH <sub>2</sub> & butyl 2CH <sub>2</sub>
20	$\delta$ 1.35	sextuplet	2H	butyl 3CH <sub>2</sub>
	$\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
	$\delta$ 1.14	multiplet	30H	propoxylate 3CH <sub>3</sub>
	$\delta$ 0.92	triplet J=7.3Hz	3H	butyl 4CH <sub>3</sub>
	$\delta$ 0.88	triplet J=7.0Hz	3H	oleyl 18CH <sub>3</sub>

25

**Oleyl 20 propylene oxide**

	$\delta$ 5.34	multiplet	2H	oleyl 9 & 10CH
	$\delta$ 4 - 3	multiplet	62H	oleyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
	$\delta$ 2.01	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
30	$\delta$ 1.56	multiplet	2H	oleyl 2CH <sub>2</sub>
	$\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
	$\delta$ 1.14	multiplet	60H	propoxylate 3CH <sub>3</sub>
	$\delta$ 0.88	triplet J=6.9Hz	3H	oleyl 18CH <sub>3</sub>

35 **Oleyl 20 propylene oxide end-capped butyl ether**

	$\delta$ 5.34	multiplet	2H	oleyl 9 & 10CH
	$\delta$ 4 - 3	multiplet	64H	butyl 1CH <sub>2</sub> , oleyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
	$\delta$ 2.02	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
40	$\delta$ 1.55	multiplet	4H	oleyl 2CH <sub>2</sub> & butyl 2CH <sub>2</sub>
	$\delta$ 1.35	sextuplet	2H	butyl 3CH <sub>2</sub>

$\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
$\delta$ 1.14	multiplet	60H	propoxylate 3CH <sub>3</sub>
$\delta$ 0.92	triplet	J $\approx$ 7.3Hz 3H	butyl 4CH <sub>3</sub>
$\delta$ 0.88	triplet	J $\approx$ 7.0Hz 3H	oleyl 18CH <sub>3</sub>

5 **Isostearyl (2-hexyl-dodecan-1-ol) 10 propylene oxide**

$\delta$ 4 - 3	multiplet	32H	dodecyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
$\delta$ 1.56	multiplet	2H	dodecyl 2CH <sub>2</sub>
$\delta$ 1.26	mutliplet	27H	dodecyl 3 - 11CH <sub>2</sub> , 6CH & hexyl 1 - 5CH <sub>2</sub>
$\delta$ 1.14	multiplet	30H	propoxylate 3CH <sub>3</sub>
10 $\delta$ 0.88	triplet	J $\approx$ 6.9Hz 3H	decyl 12CH <sub>3</sub> & hexyl 6CH <sub>3</sub>

**Isostearyl (2-hexyl-dodecan-1-ol) 20 propylene oxide**

$\delta$ 4 - 3	multiplet	62H	dodecyl 1CH <sub>2</sub> & propoxyl 1CH <sub>2</sub> & 2CH
$\delta$ 1.56	multiplet	2H	dodecyl 2CH <sub>2</sub>
$\delta$ 1.26	mutliplet	27H	dodecyl 3 - 11CH <sub>2</sub> , 6CH & hexyl 1 - 5CH <sub>2</sub>
15 $\delta$ 1.14	multiplet	60H	propoxylate 3CH <sub>3</sub>
$\delta$ 0.88	triplet	J $\approx$ 6.9Hz 3H	decyl 12CH <sub>3</sub> & hexyl 6CH <sub>3</sub>

**Olelyl 10 ethylene oxide end-capped butyl ether**

$\delta$ 5.35	multiplet	2H	oleyl 9 & 10CH
$\delta$ 3.65	singlet	32H	polyethoxyl mid chain CH <sub>2</sub>
20 $\delta$ 3.63	multiplet	4H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OR
$\delta$ 3.58	multiplet	4H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OR
$\delta$ 3.46	triplet	J $\approx$ 6.5Hz 2H	butyl 1CH <sub>2</sub>
$\delta$ 3.46	triplet	J $\approx$ 6.5Hz 2H	oleyl 1CH <sub>2</sub>
$\delta$ 2.01	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
25 $\delta$ 1.57	multiplet	4H	oleyl 2CH <sub>2</sub> & butyl 2CH <sub>2</sub>
$\delta$ 1.35	sextuplet	2H	butyl 3CH <sub>2</sub>
$\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
$\delta$ 0.92	triplet	J $\approx$ 7.3Hz 3H	butyl 4CH <sub>3</sub>
$\delta$ 0.88	triplet	J $\approx$ 7.0Hz 3H	oleyl 18CH <sub>3</sub>

30 **Olelyl 20 ethylene oxide end-capped butyl ether**

$\delta$ 5.35	multiplet	2H	oleyl 9 & 10CH
$\delta$ 3.65	singlet	72H	polyethoxyl mid chain CH <sub>2</sub>
$\delta$ 3.63	multiplet	4H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OR
$\delta$ 3.58	multiplet	4H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OR
35 $\delta$ 3.46	triplet	J $\approx$ 6.5Hz 2H	butyl 1CH <sub>2</sub>
$\delta$ 3.46	triplet	J $\approx$ 6.5Hz 2H	oleyl 1CH <sub>2</sub>
$\delta$ 2.01	multiplet	4H	oleyl 8 & 11CH <sub>2</sub>
$\delta$ 1.57	multiplet	4H	oleyl 2CH <sub>2</sub> & butyl 2CH <sub>2</sub>
$\delta$ 1.35	sextuplet	2H	butyl 3CH <sub>2</sub>
40 $\delta$ 1.26	mutliplet	22H	oleyl 3 - 7 & 12 - 17CH <sub>2</sub>
$\delta$ 0.92	triplet	J $\approx$ 7.3Hz 3H	butyl 4CH <sub>3</sub>
$\delta$ 0.88	triplet	J $\approx$ 7.0Hz 3H	oleyl 18CH <sub>3</sub>



**Oleic acid 10 ethylene oxide end-capped methyl ether**

	δ5.33	multiplet		2H	oleoyl 9 & 10CH
	δ4.22	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OC=O
	δ3.70	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OC=O
5	δ3.65	singlet		34H	polyethoxyl mid chain CH <sub>2</sub>
	δ3.55	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>
	δ3.38	singlet		2H	-OCH <sub>3</sub>
	δ2.33	triplet	J≈7.5Hz	2H	oleoyl 2CH <sub>2</sub>
	δ2.01	multiplet		4H	oleoyl 8 & 11CH <sub>2</sub>
10	δ1.62	multiplet		2H	oleyl 3CH <sub>2</sub>
	δ1.28	mutliplet		20H	oleyl 4 - 7 & 12 - 17CH <sub>2</sub>
	δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH <sub>3</sub>

**Oleic acid 20 ethylene oxide end-capped methyl ether**

	δ5.33	multiplet		2H	oleoyl 9 & 10CH
15	δ4.22	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OC=O
	δ3.70	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OC=O
	δ3.65	singlet		74H	polyethoxyl mid chain CH <sub>2</sub>
	δ3.55	triplet	J≈4.9Hz	2H	polyethoxyl -OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>
	δ3.38	singlet		2H	-OCH <sub>3</sub>
20	δ2.33	triplet	J≈7.5Hz	2H	oleoyl 2CH <sub>2</sub>
	δ2.01	multiplet		4H	oleoyl 8 & 11CH <sub>2</sub>
	δ1.62	multiplet		2H	oleyl 3CH <sub>2</sub>
	δ1.28	mutliplet		20H	oleyl 4 - 7 & 12 - 17CH <sub>2</sub>
	δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH <sub>3</sub>

25 **EXAMPLES 11 to 14**

An agrochemical composition was prepared containing 0.2 % v/v of an adjuvant in a track sprayer containing fluazifop P butyl emulsified at one of four different concentrations. Weeds which had been grown to the 2.3 leaf stage were sprayed using volumes of 200 l/ha. Each sample was replicated three times. The following weed species were tested:-

- 30 AVEFA *Avena fatua* (wild oats)  
 LOLRI *Lolium rigidum* (rye grass)  
 TRZAW *Triticum aestivum* (wheat)  
 SETVI *Setaria viridis* (green foxtails)

Activity was measured 21 days after treatment and was compared with a standard  
 35 composition containing only fluazifop-p-butyl. The concentration required to provide 90% weed kill was calculated and is given in TABLE 1 below together with the mean ED90 across the species.

TABLE 1

ED90 Values (g/ha) for Adjuvants of the Invention with Fluazifop-p-butyl

Adjuvant	AVEFA	LOLRI	TRZAW	SETVI	Mean (g/ha)
Oleyl 20E Bu Ether	19.5	27.5	21.4	16.5	21.2
Oleic 10E Me Ether	16.7	34.8	28.4	15.8	23.9
Oleyl 10P Bu Ether	19.8	34.9	29.2	16.7	25.2
Oleyl 20P Bu Ether	23.4	48.6	32.2	19	30.8
No Adjuvant	36.7	81.9	66.6	45.8	57.8

5

## EXAMPLES 15 to 25

Further adjuvants of the present invention were tested for activity in combination with fluzifop-p-butyl. Activity (% weed kill) was measured 21 days after treatment and is given as a mean of 3 replicates and 4 rates of fluazifop-p-butyl. All adjuvants were applied at 0.2% v/v. The results are given in Table 2 in comparison with a corresponding

10 composition containing no adjuvant.

TABLE 2

Mean Activity (%)

Adjuvant	TRZAW	SETVI	LOLRI	AVEFA	Mean over all species
No adjuvant	19.3	58.2	37.1	62.4	44
Isostearyl 20 PO	37.3	80.9	52.5	58	57
Oleyl 20 PO Bu ether	38.8	75.9	46	67.4	57
Oleyl 20 PO	53.3	80.4	36.3	70.6	60
Oleyl 20 EO Me ether	52.1	74.6	54.9	72.3	63
Isostearyl 10 PO	53.8	81.8	51.8	67.8	64
Oleyl 10 PO Bu ether	45.8	84.2	54.4	71.4	64
Oleyl 10 EO Me ether	56.1	78.4	56.2	71.3	66
Oleyl 10PO	54.3	84.6	55.9	72.6	67
Oleyl 10 EO Bu ether	56	85.6	56.5	73.3	68
Oleyl 20 EO Bu ether	59.3	78.1	68.8	76.1	71

## EXAMPLES 26 and 27

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The indicated adjuvants were evaluated in combination with a thin leaved grass herbicide 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester. The weeds were sprayed at the

growth stages shown in the table with pesticide emulsions using a track sprayer and volumes of 200 l/ha. The adjuvants were added at 5% v/v as tank mix additives. Each result is the average of two replicates.

Treatment	Rate gai/ha	ALOMY	APESV	AVEFA	LOLMU	PHAPA	Mean All Weeds
No Adjuvant	5	5	5	0	0	0	2
	7.5	13	5	0	0	5	5
	10	23	3	0	25	3	11
0.5% Oleyl 10PO	5	55	23	70	33	23	41
	7.5	70	89	96	60	98	83
	10	92	98	98	80	99	93
0.5% Oleyl 10EO butyl capped	5	53	53	89	91	93	76
	7.5	75	97	98	98	96	93
	10	88	98	99	93	99	95

- 5
- APESV (Apera Spica-Venti)  
PHAPA (Phalaris paradoxa)

EXAMPLE 28

This example demonstrates the improvement in the biological activity of the fungicide azoxystrobin when applied with one of the novel adjuvants in glasshouse tests.

10

The results quoted are the mean percentage disease control from four replicates on barley inoculated with *Puccinia recondita*. Azoxystrobin was applied from the commercial formulation Quadris 25 SC which was diluted to the strengths shown in the table. The adjuvant was added as a 0.5 % v/v tank mix.

Azoxystrobin mgai/l	No adjuvant control	Oleyl 20E Butyl capped
2.5	10.5	90.5
1.25	1.8	82.7
0.625	2.3	66.5
0	0	5.9

## CLAIMS

1. An adjuvant having the formula (I)



- 5 wherein  $R_1$  is a  $C_{16}$  to  $C_{20}$  straight or branched chain alkyl or alkenyl group,  $R_2$  is ethyl or isopropyl,  $n$  is from 8 to 30 and  $m$  is 0 or 1 and when  $R_2$  is ethyl,  $R_3$  is a  $C_1$  to  $C_7$  alkyl group and when  $R_2$  is isopropyl,  $R_3$  is hydrogen or a  $C_1$  to  $C_7$  alkyl group, provided that when  $R_1$  is oleyl,  $R_2$  is isopropyl and  $R_3$  is hydrogen,  $n$  is not 10.
2. An adjuvant according to claim 1 wherein  $R_1$  is an alkenyl group having from 1 to 3  
10 double bonds.
3. An adjuvant according to claim 1 or 2 wherein  $R_1$  is a  $C_{18}$  branched chain alkyl or  $C_{18}$  alkenyl group.
4. An adjuvant according to claim 3 wherein  $R_1$  is oleyl or isostearyl
5. An adjuvant according to any of the preceding claims wherein  $m$  is 0.
- 15 6. An adjuvant according to any of the preceding claims wherein  $n$  is from 10 to 20.
7. An adjuvant according to any of the preceding claims wherein when  $R_2$  is not hydrogen it is methyl or butyl.
8. Oleyl 10 propylene oxide end-capped butyl ether, oleyl 20 propylene oxide, oleyl 20 propylene oxide end-capped butyl ether, isostearyl 10 propylene oxide, isostearyl 20  
20 propylene oxide, oleyl 10 ethylene oxide end-capped butyl ether, oleyl 20 ethylene oxide end-capped butyl ether, oleic acid 10 ethylene oxide end-capped methyl ether, and oleic acid 20 ethylene oxide end-capped methyl ether.
9. An agrochemical composition comprising an adjuvant according to any of the preceding claims.
- 25 10. An agrochemical composition comprising a herbicide or fungicide and an adjuvant having the formula (I)
- $$R_1 - (CO)_m - O - [-R_2O-]_n - R_3 \quad (I)$$
- wherein  $R_1$  is a  $C_{16}$  to  $C_{20}$  straight or branched chain alkyl or alkenyl group,  $R_2$  is ethyl or isopropyl,  $n$  is from 8 to 30 and  $m$  is 0 or 1 and when  $R_2$  is ethyl,  $R_3$  is a  $C_1$  to  $C_7$  alkyl group  
30 and when  $R_2$  is isopropyl,  $R_3$  is hydrogen or a  $C_1$  to  $C_7$  alkyl group.
11. An agrochemical composition according to claim 10 or 11 being encapsulated in a microcapsule.

12. An agrochemical composition according to any of claims 10 to 12 wherein the agrochemical is fluazifop-p-butyl, azoxystrobin or 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester.



## INTERNATIONAL SEARCH REPORT

Interr ☐ Application No  
PCT/GB 02/03906

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N25/00 A01N25/30 A01N43/60 A01N25/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 235 300 B1 (BRUMBAUGH ERNEST H) 22 May 2001 (2001-05-22) column 2, line 15 -column 3, line 33 abstract; claims 1-4 ---	1-12
X	US 6 068 849 A (GARST ROGER H ET AL) 30 May 2000 (2000-05-30) column 1, line 51 -column 2, line 51 abstract; claims 1-15 ---	1-12
X	EP 0 968 649 A (DU PONT) 5 January 2000 (2000-01-05) page 2, line 36 -page 3, line 17 abstract; claims 1-12 --- -/--	1-12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Glomm, B

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03906

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 26472 A (HENKEL CORP) 3 June 1999 (1999-06-03) page 2, line 4 -page 3, line 21 abstract; claims 1-6 ---	1-12
X	WO 98 35553 A (HARTMANN FRANK DIRK JOZEF ;REEKMANS STEVEN IRENE JOZEF (BE); AUDA) 20 August 1998 (1998-08-20) page 1, line 10 -page 3, line 4 abstract; claims 1-3 ---	1-12
X	US 5 580 567 A (ROBERTS JOHNNIE R) 3 December 1996 (1996-12-03) column 2, line 55 -column 4, line 9 abstract; claims 1-19 ---	1-12
X	US 5 393 791 A (ROBERTS JOHNNIE R) 28 February 1995 (1995-02-28) column 2, line 58 -column 4, line 24 abstract; claims 1-20 -----	1-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/03906

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6235300	B1	22-05-2001	AU 2506400 A WO 0042847 A1	07-08-2000 27-07-2000
US 6068849	A	30-05-2000	AU 740063 B2 AU 8388598 A BR 9811277 A CN 1267188 T EP 1018870 A1 JP 2001510142 T NZ 502414 A TR 200000308 T2 WO 9903343 A1 ZA 9806218 A	25-10-2001 10-02-1999 29-08-2000 20-09-2000 19-07-2000 31-07-2001 01-02-2002 21-09-2000 28-01-1999 02-02-1999
EP 0968649	A	05-01-2000	EP 0968649 A1	05-01-2000
WO 9926472	A	03-06-1999	AU 1373999 A BR 9815109 A CA 2311382 A1 EP 1033911 A1 JP 2001523690 T PL 340691 A1 SK 7802000 A3 TR 200001487 T2 WO 9926472 A1 ZA 9810646 A	15-06-1999 10-10-2000 03-06-1999 13-09-2000 27-11-2001 26-02-2001 07-11-2000 23-10-2000 03-06-1999 20-05-1999
WO 9835553	A	20-08-1998	AU 733973 B2 AU 6222698 A BR 9807342 A CN 1247452 T EP 0959681 A1 WO 9835553 A1 JP 2001511801 T NZ 337036 A TR 9901940 T2 US 6413908 B1 ZA 9801030 A	31-05-2001 08-09-1998 25-04-2000 15-03-2000 01-12-1999 20-08-1998 14-08-2001 27-04-2001 22-11-1999 02-07-2002 14-08-1998
US 5580567	A	03-12-1996	US 5393791 A US 5178795 A US RE37313 E1 US 5741502 A	28-02-1995 12-01-1993 07-08-2001 21-04-1998
US 5393791	A	28-02-1995	US 5178795 A US RE37313 E1 US 5580567 A US 5741502 A	12-01-1993 07-08-2001 03-12-1996 21-04-1998